Kinetics and Mechanism of Replacement of Nitrosobenzene in the Pentacyano(nitrosobenzene)ferrate(II) Ion by Cyanide Ion

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The rate of replacement of nitrosobenzene by cyanide ion in the complex $[Fe(CN)_5(PhNO)]^{3-}$ increases non-linearly with the cyanide-ion concentration, reaching an asymptotic value at $[CN^-]$ *ca.* 2×10^{-3}M in $1·5 \times 10^{-4}$M complex solution. A limiting S_N1 mechanism is proposed.

THERMAL decomposition of hexacyanoferrate(II) ion is a slow reversible process (1). The rate of the forward

$$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_5H_2O]^{3-} + CN^- \quad (1)$$

reaction has been followed spectrophotometrically[1] in the presence of nitrosobenzene, which reacts with the aquo-complex according to the overall equation (2).

$$[Fe(CN)_5H_2O]^{3-} + PhNO \rightleftharpoons [Fe(CN)_5(PhNO)]^{3-} + H_2O \quad (2)$$

The violet nitrosobenzene complex $[Fe(CN)_5(PhNO)]^{3-}$ has a maximum absorption at 528 nm in aqueous solution. In the present study, the rate of replacement of nitrosobenzene by cyanide ion in this complex has been measured in order to elucidate the reaction mechanism.

RESULTS AND DISCUSSION

Cyanide ion reacts with the pentacyano(nitrosobenzene)ferrate(II) complex according to equation (3).

$$[Fe(CN)_5(PhNO)]^{3-} + CN^- \rightleftharpoons [Fe(CN)_6]^{4-} + PhNO \quad (3)$$

The rate of reaction was followed spectrophotometrically at 528 nm and 50 °C. Specific rates were determined as $k = (2·303/t) \log_{10} (A_0/A_t)$, where A_0 and A_t are the optical densities of the violet complex at times 0 and t, respectively. Reproducible values were obtained when the cyanide-ion concentration was in at least a two-fold excess over that of the complex, *e.g.* at $[KCN] = 3 \times 10^{-4}$M and $[Complex] = 1·5 \times 10^{-4}$M the specific rate at 50 °C was $(5·36 \pm 0·32) \times 10^{-5}$ s^{-1} (the uncertainty is the standard deviation of the mean of twelve measurements). At higher cyanide-ion concentrations the accuracy is even better. At equivalent concentrations of the complex and cyanide ion, the rate steadily decreased throughout a particular run. Results are given in Figure 1. Hexacyanoferrate(II) ions produced in the reaction were determined spectrophotometrically after oxidation with hydrogen peroxide in weakly acidic solution (see Experimental section). The analysis showed that, with a five-fold excess of cyanide ions, 80 mole % of the complex $[Fe(CN)_5(PhNO)]^{3-}$ was converted to hexacyanoferrate(II) ion.

At zero cyanide-ion concentration, the disappearance of the violet nitrosobenzene complex is due to aquation. The reaction rate increases non-linearly with cyanide-ion concentration reaching an asymptotic value at $[CN^-]$ *ca.* 2×10^{-3}M in a $1·5 \times 10^{-4}$M solution of the complex. Figure 1 illustrates the specific rates of reaction determined in the presence and absence of 0·01M-sodium perchlorate. It is clear that the levelling off of the curve is not caused by a salt effect. Even at $I = 2$M (with a 13 000-fold excess of KNO_3 over the complex), the rate of reaction decreased by *ca.* 20% only. Therefore all the data in Figure 1 were used for evaluation of the kinetic parameters. Clearly the reaction is not a simple second-order process, since the rate becomes independent of cyanide-ion concentration when cyanide ions are present in *ca.* ten-fold excess over the complex.

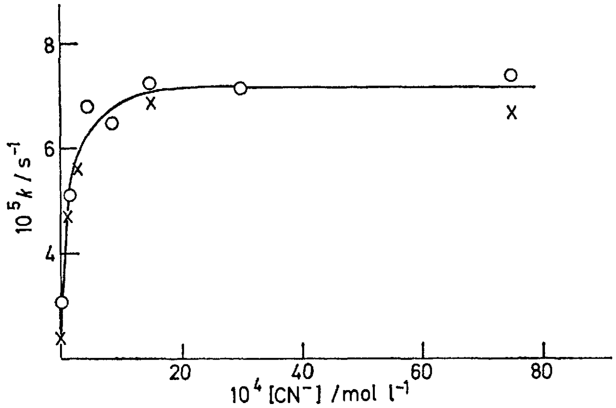

FIGURE 1 Cyanide-ion dependence of the rate of replacement of PhNO by CN^- ion in 0·00015M-$Na_3[Fe(CN)_5(PhNO)]$ at 50 °C; in the absence (×) and presence (○) of 0·01M-$NaClO_4$

Furthermore, a second-order reaction between the nitrosobenzene complex and cyanide ion, according to Brønsted's theory, would be expected to show a positive salt effect, both ions being negatively charged.

Substitution reactions of octahedral complexes generally occur by a predominantly bond-breaking mechanism, but an associative mechanism has been proposed for the reaction of some Schiff base-,[2a] tris(1,10-phenanthroline)-,[2b] and tris(2,2'-bipyridine)-iron(II)[2c] complexes with OH^- and cyanide ions. On the other hand in the reaction of the $[Fe(bipy)_2(CN)_2]$ complex (bipy = 2,2'-bipyridine) with 1,10-phenanthroline the rate-determining step is loss of the first 2,2'-bipyridine molecule.[2d] In the present case, the five cyanide groups in the $[Fe(CN)_5(PhNO)]^{3-}$ complex cause a high electron density

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[2] (*a*) J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc.* (*A*), **1971**, 44; (*b*) J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133; (*c*) D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, **79**, 2728; J. Burgess, *J.C.S. Dalton*, 1972, 1061; (*d*) J. Burgess, *J.C.S. Dalton*, 1972, 203.

at the iron centre, which will weaken the Fe–PhNO bond. Haim and Wilmarth[3] have shown that a dissociative mechanism operates in the reaction of the $[Co(CN)_5H_2O]^{2-}$ complex with SCN^- and N_3^- ions. Such a mechanism has also been confirmed in replacement reactions of substituted sulphitocobalt(III) complexes,[4] the rates of which are markedly accelerated by the sulphito-ligand.

In the pentacyano-intermediate of the present reaction an increase in bond angles due to the negative charges of the cyanide ligands would be expected to stabilize the intermediate to the extent that it becomes sufficiently long-lived to exhibit a selective reactivity toward different nucleophiles, the reactivity being independent of the leaving group. The following equilibria should be considered. Since the intermediate $[Fe(CN)_5]^{3-}$ is thermodynamically unstable, the steady-

$$[Fe(CN)_5(PhNO)]^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + PhNO \qquad (4)$$

$$[Fe(CN)_5]^{3-} + CN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(CN)_6]^{4-} \qquad (5)$$

$$[Fe(CN)_5]^{3-} + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe(CN)_5H_2O]^{3-} \qquad (6)$$

state approximation is applicable to equation (7) which leads to the rate law (8), where $k_3' = k_3[H_2O]$. Terms containing k_{-1} and k_{-2} are very small because the reverse of reaction (4) is unimportant and aqueous solutions of

$$-d[Fe(CN)_5(PhNO)^{3-}]/dt = k_1[Fe(CN)_5(PhNO)^{3-}] - k_{-1}[Fe(CN)_5{}^{3-}][PhNO] \qquad (7)$$

$$-d[Fe(CN)_5(PhNO)^{3-}]/dt = \{k_1k_2[Fe(CN)_5(PhNO)^{3-}][CN^-] + k_1k_3'[Fe(CN)_5(PhNO)^{3-}] - k_{-1}k_{-3}[Fe(CN)_5H_2O^{3-}][PhNO] - k_{-1}k_{-2}[Fe(CN)_6{}^{4-}][PhNO]\}/(k_{-1}[PhNO] + k_2[CN^-] + k_3') \qquad (8)$$

hexacyanoferrate(II) ions are very stable in the absence of light. The term $k_1k_3'[Fe(CN)_5(PhNO)^{3-}]$ is negligible compared to the term $k_1k_2[Fe(CN)_5(PhNO)^{3-}][CN^-]$ because the major product of the reaction is the complex $[Fe(CN)_6]^{4-}$ and not that of $[Fe(CN)_5H_2O]^{3-}$. Hence the approximate rate law is as in equation (9), from which

$$-d[Fe(CN)_5(PhNO)^{3-}]/dt = \frac{k_1k_2[CN^-][Fe(CN)_5(PhNO)^{3-}]}{k_2[CN^-] + k_3'} \qquad (9)$$

that of (10) is obtained. Figure 2 shows that on plotting $1/k_{obs}$ against $1/[CN^-]$ a straight line was actually obtained. Parameters were determined by a least-squares

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_3'}{k_1k_2[CN^-]} \qquad (10)$$

method; from the intercept, $k_1 = 0{\cdot}7 \times 10^{-4}\ s^{-1}$ at 50 °C and from the gradient $k_2/k_3' = 1{\cdot}2 \times 10^4$ showing that the intermediate $[Fe(CN)_5]^{3-}$ reacts much faster with cyanide ion than with water, as expected from the known stability of hexacyanoferrate(II) ions in solution.

The simplified rate equation (9) requires, at high cyanide-ion concentrations, the rate of reaction to become independent of $[CN^-]$, as is observed (Figure 1).

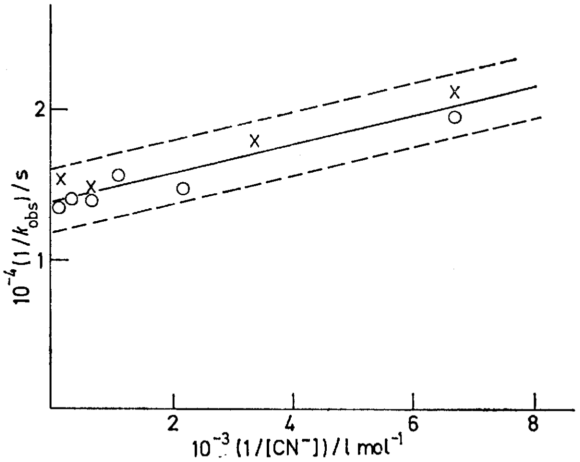

FIGURE 2 Plot of $1/k_{obs}$ against $1/[CN^-]$ using data from Figure 1. Broken lines are 95% confidence limits[5]

Thus the reaction is seen to occur *via* a limiting S_N1 mechanism. This is a particularly clear case of the latter because CN^- does not form ion pairs with the negatively charged complex.

EXPERIMENTAL

All chemicals used were of Merck analytical grade. The complex $Na_3[Fe(CN)_5(PhNO)],nH_2O$ was prepared as previously described;[1] the number of molecules of water of crystallization is dependent on the drying procedure employed. The complex was dissolved in absolute methanol with a known water content and the total amount of water in the solution determined by the Karl–Fischer method. It was found that the complex contained 4·5 molecules of water of crystallization. Iron was determined, after treatment of the complex with concentrated sulphuric acid, by titration with potassium permanganate according to the Zimmermann–Reinhardt method {Found: Fe, 12·6; C, 29·8; H, 3·2. $Na_3[Fe(CN)_5(PhNO)],4{\cdot}5H_2O$ requires Fe, 12·6; C, 29·8; H, 3·2%}. The aqueous solution of the complex was characterized by a maximum absorption at 528 nm (ε 5300 l mol⁻¹ cm⁻¹) and by a minimum at 372 nm (ε 237 l mol⁻¹ cm⁻¹). The extinction coefficients were determined for a $7{\cdot}6 \times 10^{-5}$M solution of the complex.

The product $[Fe(CN)_6]^{4-}$ was determined as follows. An aliquot portion of the reaction mixture was acidified with acetic acid (4%) and hexacyanoferrate(II) ions oxidized with hydrogen peroxide (6%) solution. The concentration of the resulting $[Fe(CN)_6]^{3-}$ ions was determined spectrophotometrically in dilute aqueous solution by measuring the optical density at 420 nm ($\varepsilon_{max.}$ 1010 l mol⁻¹ cm⁻¹). All absorption measurements were made on a Unicam SP 500 spectrophotometer (10 mm cells).

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